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AIR MONITORING NETWORK STUDY: LONG-TERM AMBIENT AIR MONITORING FOR PESTICIDES IN MULTIPLE CALIFORNIA COMMUNITIES

I. INTRODUCTION

The Department of Pesticide Regulation (DPR) is the public agency responsible for protecting California and its residents from adverse health effects caused by pesticide exposure. As part of DPR's mandate for "continuous evaluation" of currently registered pesticides, DPR is implementing a statewide air monitoring network for measuring pesticides in air from various rural agricultural communities. DPR evaluated 226 communities in California as candidates for the study. The communities were prioritized on pesticide use (both within 5 miles and regional use) and some demographic data. The aim is to document pesticide levels in ambient air collected from communities with higher populations of children, persons over 65, persons who work on farms and close proximity to agricultural areas with high use of pesticides.

DPR, the Air Resources Board (ARB), university researchers, and others currently conduct short-term air monitoring studies of pesticides. For example, DPR and the ARB coordinate monitoring for pesticides under California's Toxic Air Contaminant Act. In this program, two types of samples are collected. Air is monitored next to applications of specific pesticides for several days (application-site monitoring) to estimate acute exposures. Samples are also collected for several weeks in communities near high-use regions and during high-use periods (ambient monitoring) to estimate seasonal exposures. DPR extrapolates the short-term concentrations detected during several days or weeks of monitoring to estimate concentrations associated with annual and lifetime exposures. Additionally, both the application-site and ambient monitoring usually sample for single pesticides.

While similar to current ambient monitoring, the air monitoring network will supplement the toxic air contaminant monitoring by providing data for long-term exposures over several years to multiple pesticides. DPR conducted similar multiple-pesticide monitoring projects in Lompoc (Santa Barbara County) and Parlier (Fresno County). However, their duration was shorter (Lompoc 10 weeks; Parlier 12 months). DPR designed the Parlier project in part to evaluate methods and approaches that it might use for a future air monitoring network. In 2006, DPR collected air samples three times a week for one year at three community schools in Parlier. In addition, ARB monitored for several pesticides one day out of every week. Of the 35 pesticides (plus 5 pesticide breakdown products) monitored, 16 were detected (plus 3 breakdown products.) Methyl isothiocyanate (MITC), chlorpyrifos, and diazinon were detected in 84%, 64%, and 32%, respectively, of the samples collected (Wofford et al., 2009). In one air sample, the insecticide

diazinon was measured at 172 ng/m³, which exceeded the human health protection screening level of 130 ng/m³ established for diazinon. The study prompted DPR to move diazinon to the top of the high priority list for risk assessment, and to speed up the assessment of chlorpyrifos already in process.

In 2011, DPR will start the Air Monitoring Network study that will encompass monitoring ambient air for pesticides in three communities over a period of three years or longer (Segawa et al., 2010). To date, meetings have already been held to inform the general public of this project and discussions have occurred to identify sites for locating the ambient air sampling stations in the North Central Coast Air Basin, San Joaquin Valley Air Basin, and Ventura County. Like the Parlier air monitoring study, the Air Monitoring Network will monitor air from rural agricultural communities where pesticides are frequently applied.

II. OBJECTIVES

The five primary objectives of the Air Monitoring Network include:

1. Identify common pesticides in air and determine seasonal, annual, and multiple year concentrations.
2. Compare air concentrations to sub-chronic and chronic human health screening levels.
3. Track trends in air concentrations over time.
4. Estimate cumulative exposure to multiple pesticides with common modes of action.
5. Correlate air concentrations with pesticide use and local weather patterns.

III. PERSONNEL

DPR's standard project organization and responsibilities are described in SOP ADMN002.01 (Segawa, 2003). This project is under the overall management of Randy Segawa, Environmental Program Manager 1, DPR-Environmental Monitoring Branch, (916) 324-4137, rsegawa@cdpr.ca.gov. Other key personnel assigned to this project include:

Project Supervisor:	Pam Wofford, Project Supervisor, Senior Environmental Scientist, DPR (916) 324-4297 pwofford@cdpr.ca.gov
Project lead:	Edgar Vidrio
Field Coordinator:	Jessica Mullane
Senior Scientist	Pesticide Registration and Evaluation Committee
Statistician:	Jing Tao
Risk Evaluation:	Jay Schreider
Laboratory Liaison:	Sue Peoples
Analytical Laboratory:	California Department of Food and Agriculture (CDFA), Center for Analytical Chemistry

IV. STUDY PLAN

A. General Overview

DPR will monitor one location in each of three communities, collecting one set of 24-hour samples each week. In 2006, DPR conducted a year-long ambient air monitoring study in Parlier. This plan is based on an evaluation of results from a one-year study in Parlier that included air monitoring at three locations, three days each week. The Parlier data indicated that monitoring a single location once a week will provide adequate data to estimate long-term concentrations. DPR analyzed the number of positive samples for the three most frequently detected pesticides: chlorpyrifos, diazinon, and methyl isothiocyanate (MITC). The air concentrations were not normally distributed, so standard statistical techniques could not be used. However, the Parlier data showed little difference between the three Parlier monitoring locations in the frequency of detection. Similarly, there was little difference in frequency of detections between odd and even weeks, and days of the week. Based on this analysis, it is likely that sampling at one location in each community, one day each week, will provide adequate data to characterize seasonal and long-term exposure.

Monitoring sites must meet the following minimum criteria:

- The location of sample collection meets all U.S. EPA ambient air siting criteria
 - 2 to 15 meters above ground
 - At least 1 meter horizontal and vertical distance from supporting structure
 - Should be at least 20 meters from trees
 - Distance from obstacles should be at least twice the obstacle height
 - Unobstructed air flow for 270°
- Accessible to sampling personnel during time of sampling
- Accessible to electrical outlets
- Secure from equipment loss or tampering
- Permission of site operator/owner

Preferred monitoring sites also meet the following criteria:

- School, day care center, or other “sensitive site”
- Located on the edge of the community and/or adjacent to agricultural fields

B. Communities Selected for Monitoring

DPR has sufficient resources to monitor three communities. DPR selected communities based on objective data, using criteria that can be quantified, validated, and verified. This provides a transparent and fair selection process. DPR evaluated 226 communities in the following areas for monitoring:

- North Central Coast air basin (48 communities)
- San Joaquin Valley (161 communities)
- Ventura County (17 communities)

DPR evaluated and rated each of the communities using the following criteria:

- 1) Use of pesticides listed above
 - b. Use within the community (community zone)
 - c. Use between the community boundary and 1 mile of the community (local zone)
 - d. Use within 1 to 5 miles of the community (regional zone)
- 2) Demographic criteria
 - a. Population density of people under age 18
 - b. Population density of people older than 65
 - c. Population density of people older than 5, with disabilities
 - d. Population density of people employed in farming, fishing, or forestry (indicator of farmworkers)

Some communities in proximity to each other have similar ratings, particularly for pesticide use due to similar cropping patterns. To evaluate a variety of pesticide exposures, DPR selected communities that represent different pesticide use patterns.

DPR selected communities with higher use of the pesticides within the zones listed above because they will likely have higher air concentrations. The demographic groups noted above represent subpopulations DPR considers in its risk assessments. See Neal, et al. (2010) for further details on the method used to select the communities.

Based on the criteria above, DPR selected the following three communities for the air monitoring network:

- Ripon (San Joaquin County, approximately 20 miles south of Stockton)
- Salinas (Monterey County, approximately 60 miles south of San Jose)
- Shafter (Kern County, approximately 20 miles northwest of Bakersfield)

These three communities provide a good geographic distribution and have relatively high use for most of the selected pesticides. At least one of these three communities is rated 4 (top quarter) for use of each selected pesticide, except dicofol, diuron, endosulfan, simazine, and sodium tetrathiocarbonate. Salinas and Shafter also have complementary air monitoring stations. Salinas also has a high demographic rating and a community health study in progress.

Ripon

Is a small city (4.2 square miles in area) located approximately 20 miles south of Stockton in San Joaquin County. The elevation is 69 feet, with approximately 13.8 inches of precipitation annually. Average temperatures during summer range from 60° – 94° and 47° – 62° F. Based on US Census data, the estimated population in 2000 was 10,146, of which 25.7% was below 18 years and 12.4% was 65 and above. Almond orchards, grapes and field crops are the major crops surrounding the community.

The monitoring site is located in an open area behind the Police Station on N. Wilma Ave near the western side of the middle of the city.

Shafter

Shafter is a small city (18 square miles in area) located approximately located 18 miles west-northwest of Bakersfield in Kern County. The elevation is 351 feet, with approximately 7 inches of precipitation annually. Average temperatures during summer range from 59° – 99° F and 35° – 64° F in winter. In 2000, the population was 12,736 of which 25.7% was below 18 and 12.4% was above 65 years of age. The major crops in the immediate area around Shafter are almonds, grapes, and alfalfa some field crops.

The monitoring site is located near a city well near Shafter High School in the northeastern edge of the city.

Salinas

Salinas is located in Monterey County approximately 15 north-east of Monterey and encompasses a total area of 22.8 square miles. In 2000, Salinas had a population of 151,060 of which 25.7% was below 18 years of age and 12.4% was above 65. The average rainfall is approximately 14.5 inches, and the typical daily highs range from 52° F in the winter to around 72° F in the summer and highs lows from 40° F in the winter to 51° F in the summer. Heavy morning fog often occurs during summer months. Salinas is surrounded mainly by strawberries, lettuce and other field crops.

The monitoring site is located at the Salinas Airport in the south-eastern section of the City.

Maps of the monitoring locations and reported pesticide use within 5 miles of each community selected for monitoring are located in Appendix A. The maps present the reported use of fumigants, organophosphates, and other pesticides around each community. The weather for each community during 2009 is included on the maps. The windroses indicate the direction the wind is blowing from.

C. Air Sampling Equipment and Method

The sample will have a minimum of 3 ft horizontal and vertical distance from its supporting structure, be at least 65 ft from trees, have a distance from obstacles at least twice the obstacle height, and have unobstructed air flow for 270° around the air sampling equipment. A protective shelter will be placed at each air sampling location. The shelter will house an Airchek HV30 pumps, (SKC Inc® catalog #228-030), SKC Inc® personal sample pumps (if necessary), and SilcoCan® canisters (Restek cat. no. 24142-65). The shelter will prevent damage to air sampling equipment from sunlight, rainfall, and fog during the long-term monitoring study.

The Airchek pumps will pull air at a rate of 15 L/min through a hand-packed glass sample tube or Teflon® cartridge containing 30 mL of XAD-4 sorbent resin material. SKC Inc® personal sample pumps will be set to a flow of 1.5L/min and use a manufactured pre-packed 200/1800 mg coconut charcoal tube with sealed glass end tips (SKC Inc, # 226-16-02) for MITC or a XAD-4 tube (SKC Inc, # 226-175) for chloropicrin set at a flow of 50ml/min. Canisters will operate with a flow controller set to collect a 24-hr sample. All air sampling equipment will be operated for 24 hr air collection periods. The operation, calibration, and maintenance of the SKC Inc® pump is located in DPR's Standard Operating Procedure (SOP) EQAI001.00 (Wofford, 2001),

the SOPs for the Aircheck sample pump and canisters are in progress. Air sampler flow rates will be measured using a DryCal ® flow meter at the beginning of the sampling period and the end of sampling period. The weekly starting day will vary through the week and if possible will be randomly selected.

Sample labels printed with the study number and a sample tracking number will be secured to the outside of all sample tubes and canisters. When air sampling commences at each monitoring site, the sample tracking number, date, time, staff initials, weather conditions, and air sampler flow rate will be documented on a chain of custody (COC) form as presented in SOP ADMN006.01 (Ganapathy, 2004). At the end of each sampling period staff will record the date, time, staff initials, and ending flow rate on the COC form. Weather conditions and other pertinent information that may affect sample results will be recorded on the COC or in a field note book.

Once samples are collected, open tube or cartridge ends will be tightly capped with appropriate end caps and the canister's flow will be closed. Canisters will be transported at ambient conditions. All sample tubes or cartridges will be placed into an insulated storage container containing dry ice and remain frozen until transported to the West Sacramento facility where they will be checked-in and placed into a freezer until delivered to the laboratory for analysis. Sample handling-shipping and tracking procedures will be followed as defined in DPR's SOP QAQC004.1 (Jones, 1999) and SOP QAQC003.02 (Ganapathy, 2005), respectfully.

D. Field Sampling Quality Control

Three types of quality control samples will be routinely collected in the field over the course of the air monitoring study; trip blanks, fortified field spikes, and co-located duplicate samples. A trip blank sample is a "blank" sample tube or canister containing no pesticide residue. Upon collection of all field samples for that week, the end caps of a trip "blank" are momentarily removed or broken and the tube is then immediately re-capped. The canisters remain unopened. Air is not pulled through any of the trip blank samples. The "blank" samples are placed with the study samples and transported together until receipt at the West Sacramento facility. If pesticide residue is detected in any of the blank samples, action will take place to reassess field and laboratory procedures.

Fortified field spikes are sample tubes that have an added known quantity of pesticides prepared and added by the laboratory. Following laboratory preparation, field spikes are transported at the beginning of the week's sampling period where they are stored on dry ice until needed. Fortified field spike tubes are then placed on the second set of air sampling pumps housed in the portable shelter and operated under the same conditions and time-frame as the primary air sampler pumps.

Comparison of the fortified sample and field sample pesticide recovery at the same monitoring location from the same type of air sampling pump will provide information on any change in the ability to recover the pesticides under field conditions. Should fortified field spike pesticide recoveries fall outside the preset recovery control limits then a reassessment of the field and laboratory procedures is conducted.

Duplicate samples are collected adjacent to the study samples under the same conditions and time-frame as the primary air sampler. Pesticide recovery from the duplicate and primary samples is used to evaluate laboratory analytical precision; samples with greater than 50% difference in pesticide residue concentration will result in reassessment of the field and laboratory procedures.

DPR considers data to be valid if it originates from an air sampler pump that displays less than a 20% difference from the observed starting and ending flow rate. A canister sample is considered to be valid if the pressure remaining in after sampling is below -5 inches Hg.

One of the three types of quality control sample will be collected at one site every other week. At the end of the sampling year this will result in at least eight of each type, or equal to 16 percent of the number of samples collected.

An ARB quality assurance team will conduct a field audit of the sampler air flow rates.

E. Meteorological Monitoring

When available, meteorological data can be electronically downloaded from the National Weather Service, California Irrigation Management Information Systems (CIMIS) stations or from the Air Resources Board (ARB) weather stations located adjacent to monitored communities. All weather stations collect hourly data on wind speed and direction, air temperature, and relative humidity. The CIMIS stations collect additional weather and environmental information including precipitation, solar radiation, barometric pressure, dew point, and soil temperature. The Salinas monitoring site is collocated with a National Weather Service – Automated Surface Observing Systems (ASOS) weather station.

F. Pesticide Use Reporting

Pesticide use information within a 5 mile distance of each monitored community will be gathered on a township, range, and section basis to define the agricultural boundary for detected pesticide residues within a community. Universal use reporting required by DPR directs all agricultural pesticide applicators to submit detailed pesticide application information to their County Agricultural Commissioner's office. Reported pesticide use information includes operator identification, date of application, county of application, pesticide product applied, amount of pesticide product applied, area/unit treated, site/commodity treated, field identification number, and locations using meridian, township, range, section data. Detailed pesticide information is not required for applicators applying pesticides for rights-of-way, home, industrial, or commercial use.

V. ANALYTICAL METHODS

A. Pesticides to be Monitored

DPR will monitor for most of the same pesticides as the Parlier project in 2006, based primarily on potential health risk. Higher-risk pesticides have higher priority for monitoring. Pesticides were selected based on the following criteria:

- 1) Pounds of use by area/region (indicator of exposure)
- 2) Volatility (indicator of exposure)
- 3) DPR risk assessment priority (indicator of toxicity)
- 4) Feasibility of including in multi-residue monitoring method

See Neal, et al. (2010) for further details on the method used to select the pesticides.

Multi-Pesticide Residue Analysis

Table 1 lists the pesticides that are included in the California Department of Food and Agriculture Center for Analytical Chemistry (CDFA laboratory) multi-pesticide residue analysis using XAD-4 resin as the solid phase trapping medium. Analysis includes a variety of fungicides, insecticides, herbicides, and defoliants. The breakdown products of chlorpyrifos, diazinon, dimethoate, endosulfan and malathion are also included in the multi-residue analysis method.

Volatile Organic Compound Analysis

Canisters will be analyzed for the analytes listed in Table 2 using a volatile organic compound (VOC) method similar to U.S. EPA's Method TO-15. If possible, MITC and chloropicrin will be analyzed in canister method. If the laboratory is not able to analyze in the canister method, separate samples will be collected with SKC Inc® sample tubes and will be analyzed for the separate analytes.

B. Chemical Analysis

CDFA laboratory will conduct chemical analyses of air sampling media. XAD-4 resin samples will be extracted with ethyl acetate and extracts will be analyzed for pesticide residues using gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS) methods as described in method EMON-SM-05-002 (CDFA, 2008).

SKC Inc® coconut charcoal sample tubes will be analyzed for residues of MITC as described in analytical method EMON-SM41.9 (CDFA, 2004). MITC extraction from the sorbent medium involves using carbon disulfide in ethyl acetate with subsequent analysis using GC with a nitrogen/phosphorous detector.

SKC Inc® XAD-4 sample tubes will be analyzed for residues of chloropicrin as described in CDFA Method: EM16.0 (CDFA, 1999). Each tube will be desorbed in hexane and analyzed by gas chromatograph equipped with an electron capture detector (GC/ECD) as described in the laboratory analysis section.

Canisters will be analyzed for volatile organic compounds using a method similar to United States Environmental Protection Agency's (U.S. EPA) method TO-15 (U.S. EPA, 1999).

Table 1. Target analytes in multi-pesticide residue analysis with XAD-4 resin.

<u>Pesticide</u>	<u>Product Name</u>	<u>Pesticide Group</u>	<u>Chemical Class</u>
Acephate	Orthene	Insecticide	Organophosphate
Bensulide	Prefar	Herbicide	Organophosphate
Chlorothalonil	Bravo	Fungicide	Chloronitrile
Chlorpyrifos	Dursban	Insecticide	Organophosphate
Chlorpyrifos Oxygen Analog	-		
Chlorthal-dimethyl	Dacthal	Herbicide	Phthalate
Cypermethrin	Demon	Insecticide	Pyrethroid
Diazinon	Various names	Insecticide	Organophosphate
Diazinon Oxygen Analog	-		
Dicofol	Kelthan	Insecticide	Organochlorine
Dimethoate	Cygon	Insecticide	Organophosphate
Dimethoate Oxygen Analog	-		
Diuron	Karmex	Herbicide	Urea
Endosulfan	Thiodan	Insecticide	Organochlorine
Endosulfan Sulfate	-		
EPTC	Eptam	Herbicide	Carbamate
Iprodione	Rovral	Fungicide	Dicarboximide
Malathion	Various names	Insecticide	Organophosphate
Malathion Oxygen Analog	-		
Methidathion	Supracide	Insecticide	Organophosphate
Metolachlor (S-metolachlor)	Dual	Herbicide	Chloracetanilide
Naled as dichlorvos (DDVP)	Dibrom, Vapona	Insecticide	Organophosphate
Norflurazon	Solicam	Herbicide	Pyridazinone
Oryzalin	Surflan	Herbicide	Dinitroaniline
Oxydemeton-methyl	Metasystox-R	Insecticide	Organophosphate
Oxyfluorfen	Goal	Herbicide	Diphenyl ether
Permethrin	Ambush	Insecticide	Pyrethroid
Phosmet	Imidan	Insecticide	Organophosphate
Propargite	Omite	Insecticide	Organosulfite
Simazine	Princep	Herbicide	Triazine
SSS-tributylphosphorotrithioate	DEF	Defoliant	Organophosphate
Trifluralin	Treflan	Herbicide	Dinitroaniline

Table 2. Target analytes in canister residue analysis.

<u>Pesticide</u>	<u>Product Name</u>	<u>Pesticide Group</u>	<u>Chemical Class</u>
1,3-dichloropropene	Telone, Inline	Fumigant	Halogenated organic
Acrolein	Magnacide	Algaecide	Aldehyde
Methyl Bromide		Fumigant	Halogenated organic
Sodium tetrathiocarbonate as carbon disulfide	Enzone	Fumigant	Inorganic
Methyl iodide	Midas	Fumigant	Halogenated organic
MITC*	Vapam, K-Pam, Dazomet	Fumigant	
Chloropicrin*		Fumigant	Halogenated organic

*will be collected on sample tubes until laboratory is able to include in canister method.

C. Method Detection Limit and Reporting Limit

The method detection limit (MDL) is the lowest concentration of a pesticide (analyte) that a chemical method can reliably detect. The laboratory determined the method detection limit for each analyte by analyzing a standard at a concentration with a signal to noise ratio of 2.5 to 5. The spiked matrix is analyzed at least seven times, and the method detection limit is determined by calculating the 99% confidence interval of the mean. This procedure is described in detail in U.S. EPA (1990). The limit of quantitation is set a certain factor above the method detection limit. The level of interference found in the samples determines this factor: the more interference, the higher the factor. The method detection limits and limits of quantitation for each pesticide are given in Table 3.

Table 3. Detection limits and quantitation limits for the monitored pesticides. Detection and quantitation limits are approximate for a 24-hour sample and will vary with the amount of air sampled and interferences present.

Pesticide or Breakdown product	Method Detection Limit (ng/m³)	Quantitation Limit (ng/m³)
Acephate	1.02	9.3
Acrolein	124	2,290
Bensulide	1.39	9.3
Chlorothalonil	13.7	23.1
Chloropicrin	222*	2,780*
Chlorpyrifos	5.05	23.1
Chlorpyrifos oxygen analog	2.92	9.3
Chlorthal-dimethyl	1.67	23.1
Cypermethrin	4.68	23.1
Diazinon	1.16	9.3
Diazinon oxygen analog	2.08	9.3
Dichlorvos (DDVP)	3.24	23.1
1,3-Dichloropropene	599	4,540
Dicofol	2.13	23.1
Dimethoate	2.31	9.3
Dimethoate oxygen analog	1.94	9.3
Diuron	5.14	9.3
Endosulfan	3.24	23.1
Endosulfan sulfate	4.63	23.1
EPTC	1.67	23.1
Iprodione	1.06	23.1
Malathion	2.18	23.1
Malathion oxygen analog	1.30	9.3
Metam-sodium (MITC)	5.56*	23.1*
Methidathion	1.44	9.3
Methyl bromide	396	5,810
Methyl iodide	337	5,810
Metolachlor	2.73	9.3
Norflurazon	3.75	9.3
Oryzalin	1.39	23.1
Oxydemeton-methyl	2.31	9.3
Oxyfluorfen	6.39	23.1
Permethrin	7.22	23.1
Phosmet	7.96	9.3
Propargite	3.80	23.1
SSS-tributyltriphosphorotrithioate (DEF)	1.76	9.3
Simazine	1.20	9.3
Sodium tetrathiocarbonate as Carbon disulfide	324	3,110
Trifluralin	1.67	23.1

* Limits given for sample tube analysis method. Limits will be revised when added to canister method.

D. Quality Assurance

The CDFA laboratory will follow DPR's standard laboratory quality control procedures as outlined in SOP QAQC001.00 (Segawa, 1995). Prior to the analysis of field samples, the laboratory will validate the method by analyzing a series of spikes (samples containing known amounts of pesticides) to document the precision and accuracy of the methods. Trapping efficiency tests will be performed to ensure breakthrough (pesticides not adsorbed to the sorbent tube) does not occur and to check for chemical transformation of the adsorbed pesticides. Storage stability tests will be performed to document the degradation of samples between the time of sample collection and the time of sample analysis. The laboratory will include quality control samples with each batch of field samples analyzed, including blank samples (samples containing no pesticides) to check for contamination, and spikes to check the precision and accuracy.

For each analyte, upper and lower warning and control limits are set at ± 2 and ± 3 standard deviations derived from the average percent recovery, respectively, of the above mentioned replicates. During analyses of field samples (≤ 10) quality control samples will also be submitted for analyses. This includes pesticide spiked samples to provide checks on analytical precision and accuracy and blank samples to provide information on possible contamination. Corrective action will take place if spiked quality control recovery levels fall outside the established preset limits.

VI. DATA ANALYSIS

A. Air Concentration Calculations

Pesticide concentrations in air will be calculated as 24-hr air concentrations by taking the weight of the pesticide analyte per sample medium (result from chemical analysis) and dividing this value by the volume of air pulled through the sample medium over the 24-hr sampling period. Concentrations will be reported in nanograms per cubic meter (ng/m^3). The VOC concentrations will also be presented as part per billion (ppb). Samples below the limit of detection will be treated as having one-half the detection limit, except in cases where a specific pesticide is not detected and was not applied in the 5 mile pesticide use boundary, in which case this concentration will be assumed to be zero. Samples with concentrations less than the limit of quantitation (reporting limit), but greater than limit of detection will be reported as having a "trace" concentration detected. For calculation purposes, DPR will assume that trace detections contain a concentration that is the average of the quantitation limit and the detection limit.

Estimates for pesticide exposure at the seasonal and chronic levels will be made by staff toxicologists. Seasonal exposure will be estimated for each monitored community from individual 24-hr sample results by calculating the average concentration during peak use season for each pesticide. Chronic exposure will be estimated for each community from individual 24-hr sample results by calculating the average concentration of all sample results for 1 year for each pesticide.

B. Health Evaluation Methods

DPR will compare these measured ambient air concentrations to human health screening levels to determine what, if any, action to take. No state or federal agency has established regulatory health standards for pesticides in ambient air (some agencies have developed occupational standards, or site-specific standards). Therefore, DPR in consultation with OEHHA and others has developed health screening levels for monitored pesticides to place the results in a health-based context (Table 4). Although not regulatory standards, these screening levels can be used in the process of evaluating the air monitoring results. A measured air level that is below the screening level for a given pesticide would generally not be considered to represent a significant health concern and would not generally undergo further evaluation, but also should not automatically be considered “safe” and could undergo further evaluation. By the same token, a measured level that is above the screening level would not necessarily indicate a significant health concern, but would indicate the need for a further and more refined evaluation. Significant exceedances of the screening levels could be of health concern and would indicate the need to explore the imposition of mitigation measures.

To the extent possible, the screening levels are based on toxicology values taken from existing documents. The three primary sources are risk assessments, in the form of Risk Characterization Documents (RCDs) conducted by DPR, Reregistration Eligibility Documents (REDs) completed by USEPA, and Reference Exposure Levels (RELs) established by OEHHA and peer reviewed by the Toxic Air Contaminant (TAC) Scientific Review Panel. These documents specified the studies and toxicity values to be used for various exposure scenarios (e.g. acute inhalation, chronic exposure, etc.). When REDs or RCDs are not available or appropriate values are not available, the primary source was the DPR Toxicology Database. A description of how the screening levels were calculated and the data used to determine the levels for each monitored chemical are presented in Attachment IV.

The potential health risk of a chemical(s) in air is a function of both the inherent toxicity of the chemical(s) as well as the level of exposure to the chemical(s). The potential health risk to community residents from exposure to pesticides in the air can be evaluated by comparing the air concentration measured over a specified time (e.g. 24 hours, one month, one year) with the screening level derived for a similar time (acute, seasonal, chronic). The ratio of an exposure level for a chemical (measured air concentration of a pesticide) to a reference concentration or screening level for that pesticide is called the Hazard Quotient (HQ). In this case,

$$\frac{\text{Air concentration}}{\text{Screening level}} = \text{Hazard quotient}$$

A hazard quotient is the air concentration detected expressed as the percentage of the screening level. For example, if the air concentration were 25 percent of the screening level, then the hazard quotient would be 0.25. When the hazard quotient is greater than one, the air concentration would exceed the screening level and further analysis of the data would be required.

Overexposure to pesticides can cause a variety of adverse health effects. An overview of the potential health effects for pesticides included in the monitoring is given in Attachment IV. Pesticides may exhibit toxic effects independently, or they may interact in an additive, synergistic, or antagonistic manner. As a preliminary approach, DPR will estimate risk from multiple pesticides by adding all of the hazard quotients for the individual pesticides:

$$\begin{aligned} \text{Hazard Index} = & \text{Hazard Quotient of Pesticide 1} \\ & + \text{Hazard Quotient of Pesticide 2} \\ & + \text{Hazard Quotient of Pesticide 3 ... (and so forth)} \end{aligned}$$

This approach assumes that toxicity and risk of all monitored pesticides are additive, although only a subset of the monitored pesticides (including organophosphate insecticides and oxygen analog breakdown products toxic to the nervous system) are known to act in an additive manner. U.S. EPA has developed more refined methods for analyzing cumulative impacts of pesticides, and these, the hazard quotient approach, and other avenues will be explored.

Should levels of pesticides be found above screening levels, it can trigger additional data collection and evaluation, in these communities and elsewhere. The data helps DPR to evaluate the geographic scope, timing and use factors that contributed to the air concentrations. These and other data can establish parameters of problematic residues. The data are necessary to develop effective measures to minimize or eliminate unacceptable air exposures, and are required by law to support regulatory action.

VII. EVALUATION OF RESULTS

The monitoring results will be evaluated to determine the exposure and risk from individual as well as multiple pesticides. The data will be compared to historical monitoring results from other areas. DPR will also evaluate the results and pesticide use patterns at the time of monitoring to determine possible mitigation measures, as well as other potential areas and time periods for future monitoring.

Table 4. Health screening levels for pesticides included in the monitoring.

Pesticide or Breakdown product	Acute^a Screening Level (ng/m³)	Subchronic Screening Level (ng/m³)	Chronic Screening Level (ng/m³)
Acephate	12,000	8,500	8,500
Acrolein	350	350	350
Bensulide	259,000	24,000	24,000
Chlorothalonil	34,000	34,000	34,000
Chloropicrin	491,000	2,300	1,800
Chlorpyrifos	1,200	850	510
Chlorpyrifos oxygen analog	1,200	850	510
Chlorthal-dimethyl	23,500,000	470,000	47,000
Cypermethrin	113,000	81,000	27,000
Diazinon	130	130	130
Diazinon oxygen analog	130	130	130
1,3-Dichloropropene	160,000	120,000	120,000
Dichlorvos (DDVP)	11,000	2,200	770
Dicofol	68,000	49,000	20,000
Dimethoate	4,300	3,000	300
Dimethoate oxygen analog	4,300	3,000	300
Diuron	170,000	17,000	5,700
Endosulfan	3,300	3,300	330
Endosulfan sulfate	3,300	3,300	330
EPTC	230,000	24,000	8,500
Iprodione	939,000	286,000	286,000
Malathion	112,500	80,600	8,100
Malathion oxygen analog	112,500	80,600	8,100
Metam-sodium (MITC)	66,000	3,000	300
Methidathion	3,100	3,100	2,500
Methyl bromide	820,000	35,000	3,900
Methyl iodide	185,770	261,240	87,080
Metolachlor	85,000	15,000	15,000
Norflurazon	170,000	26,000	26,000
Oryzalin	420,000	230,000	232,000
Oxydemeton-methyl	39,200	610	610
Oxyfluorfen	510,000	180,000	51,000
Permethrin	168,000	90,000	90,000
Phosmet	77,000	26,000	18,000
Propargite	14,000	14,000	14,000
SSS-tributyltriphosphorotrithioate (DEF)	8,800	8,800	b
Simazine	110,000	31,000	31,000
Sodium tetrathiocarbonate as Carbon disulfide	1,550,000	800,000	800,000
Trifluralin	1,200,000	170,000	41,000

a. Normalized to 24 hour unless otherwise noted, subchronic and chronic also normalized to 7 days a week

b. These pesticides have seasonal use only, so there is no chronic exposure.

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